Commentary on "Homogeneous nucleation of NAD and NAT in liquid stratospheric aerosols: insufficient to explain denitrification" by Knopf et al.

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Atmos. Chem. Phys. Discuss., 3, 827–833, 2003
www.atmos-chem-phys.org/acpd/3/827/

Atmospheric Chemistry and Physics Discussions

Commentary on "Homogeneous nucleation of NAD and NAT in liquid stratospheric aerosols: insufficient to explain denitrification" by Knopf et al.

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Received: 30 December 2002 – Accepted: 31 January 2003 – Published: 14 February 2003

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In a recent published paper Knopf et al. (2002) have suggested that the homogeneous freezing behavior of stratospheric aerosols, under polar winter conditions, can be simulated experimentally in large bulk phase-sized droplet samples (0.12–0.27 cm in diameter). Their hypothesis is based on the fact that a nucleus, which freezes the supercooled phase, forms within the bulk volume of a given sample, and therefore, if large bulk volumes do not freeze in the laboratory, then small volumes in particles most certainly remain unfrozen in the stratosphere. The important question to ask here is whether or not their initial hypothesis, which they have used to analyze their data, is even correct to begin with. For example, does a nucleus, which turns over the phase, forms within the bulk volume or on the surface of the supercooled phase? Some recent studies provide both experimental (Tabazadeh et al., 2002a, b) and theoretical (Djikaev et al., 2002a, b) support for the formation of the nucleus on the surface of supercooled droplets. If the nucleus in small particles forms on the surface, then can one reasonably extrapolate bulk phase results, as was done in Knopf et al. paper, to determine whether small submicron particles will freeze or not, given that significantly vast differences exist between surface-to-volume ratio of bulk-sized samples and particles. Below, I provide at least a couple of reasons as to why the approach taken by Knopf et al. to study this crystallization process is faulty at a fundamental level. Therefore, their criticism of the aerosol freezing rates (Salcedo et al.) used in the modeling study by Tabazadeh et al. (2001) is unjustified.

First, in Fig. 1 the percentage of molecules residing on the surface of a given size sample, relative to the total number of molecules present in the entire sample, is shown. As the arrow indicates, only 0.0005% of molecules in the Knopf et al. sample resided on the surface. This calculation shows that the presence of only 0.0005% of a surface-active component in their samples could have contaminated the surface layer and thus prevented the nucleation from occurring at this interface. Surface-active components preferably partition into the surface layer of an aerosol particle instead of dissolving within its bulk volume. Such components are often (not always) made of longer chain hydrocarbons and relatively higher molecular weight oxygenated organic molecules

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(see Baagi and Donaldson and references therein). Given that freezing in particles most likely initiates at the surface layer (Tabazadeh et al., 2002a, b), the surface tension at the air-solution interface is what ultimately controls the overall rate of the nucleation process. Thus, slight contamination by molecules, which preferably partition into the surface layer, can dramatically hamper the rate of the nucleation process. Since Knopf et al. have provided no experimental evidence to show that trace amounts of "sticky" surface-active molecules were not present in their samples at such low levels (<0.0005%), it is hard to imagine that their surfaces were pure enough to study this crystallization process. On the contrary, careful composition analysis of aerosols generated in the laboratory indicates that they often contain organic impurity (Middelbrook et al., 1997). Figure 1 also shows that if this crystallization process is studied using submicron particles, then significant fractions of surface active components are needed to deactivate the surface from freezing into hydrates of nitric acid. For example, for a 0.1 micron particle roughly 5% of a surface-activate component is needed to fully contaminate the surface layer. Thus, one can see through this illustration the power of conducting freezing experiments, using small particles instead of bulk-sized samples because it will be nearly impossible to purify bulk samples to a point where "sticky" surface-active organic molecules become rare entities at the surface layer. Of course, such "sticky" organic molecules that are present near the surface of the Earth, and perhaps in the environment of a terrestrial laboratory (Middelbrook et al., 1997), are relatively scarce molecules to stick to the surfaces of pristine cloud droplets in the winter polar stratosphere.

Second, it seems that the Knopf et al. study does not account for the fact that the surface layer has a different chemical composition than that of the bulk phase, mainly due to stronger surface adsorption of some components relative to others. Specifically, it has been shown that molecular nitric acid is enriched at the surface layer of aqueous solutions (Donaldson and Anderson, 1999; Yang and Finlayson-Pitts, 2001). Furthermore, our recent studies (Djikaev and Tabazadeh, 2002) also show that the level of surface enrichment of a given species in a multicomponent solution is a function of

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particle size. Thus, even if the bulk samples of Knopf et al. had pristine surfaces, which is highly unlikely, the surface layer of a bulk sample has a different chemical composition than that of an "actual" submicron particle in the stratosphere. The onset of the crystallization process in a small supercooled particle most likely initiates on the droplet surface (Tabazadeh et al, 2002a, b). Therefore, is it reasonable to investigate the freezing process of a completely different surface in the laboratory, using large sample sizes, and relate that somehow to the stratospheric particle system, as was done in the Knopf et al. study. Overall, these types of extrapolations are not physically sound, mainly because apples are being compared to oranges, and cannot help us to advance science in this research area.

Finally, for the reasons given above the Knopf et al. experimental results are faulty and are not applicable to the real atmosphere. However, the experimental rates (Salcedo et al.) used in the modeling study of Tabazadeh et al. (2001) may not be completely accurate for the reasons discussed in the Tabazadeh et al. (2002b) paper, and not for the reasons given in the Knopf et al. study.

I would like to end this commentary by stating that my main purpose for writing this letter is to advocate a need for quantitative experimental data on the freezing process of the stratospheric particle system. Such particle systems in the stratosphere are highly supercooled and they must freeze into hydrates of nitric acid if they are observed for long enough periods and if enough care is exercised in the laboratory to prepare pristine supercooled droplet samples that are representative of the real atmosphere. It is important that the rate of the stratospheric cloud freezing process is quantified through careful laboratory experiments. Once the rates are known quantitatively, then one can truly examine whether this system will freeze homogeneously or not in the polar stratosphere. Such firm conclusions, as stated in the title and the abstract of the Knopf et al. paper, are not warranted because the experimental procedure used is not up to the task to methodically and carefully examine this homogeneous freezing process. If homogeneous rates obtained from future laboratory experiments turn out to be too slow, then the next step is to look into possible heterogeneous pathways for this nucleation

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process, involving ice or perhaps other types of solid surfaces. Too many experimental and theoretical papers have been written on this subject, speculating possible formation freezing scenarios, and only carefully designed and executed future submicron "particle" laboratory experiments can properly address this lingering decade-old problem. It has been known since 1993 (Molina et al., 1993) that bulk-sized samples, containing supercooled solutions of H_2SO_4-HNO_3-H_2O, do not freeze for many hours while held at cold polar stratospheric temperatures, a finding which is identical to the one presented in the Knopf et al. paper a decade later. The only conclusion that can be drawn from bulk phase studies is that the rate of freezing in the bulk is negligible, and no conclusion can be drawn regarding the rate of freezing into hydrates of nitric acid at the surface layer of a "real" submicron stratospheric aerosol particle. I hope we all agree that it is the latter process, which may be of some interest here, and not the former one that has been studied repeatedly in the laboratory over the last decade, yielding basically the same somewhat not-so-useful conclusion.

Acknowledgement. I thank T. Koop for inviting me to join the online discussion regarding this paper. Unfortunately, at the time I was too preoccupied and could not write an interactive report on this paper. However, I did provide copies of our (then) in press manuscripts (now published in Journal of Physical Chemistry) to T. Koop. Thus, the information, upon which most of this commentary is based on, were made available to the authors of the Knopf et al. paper prior to the formal publication date of their manuscript.

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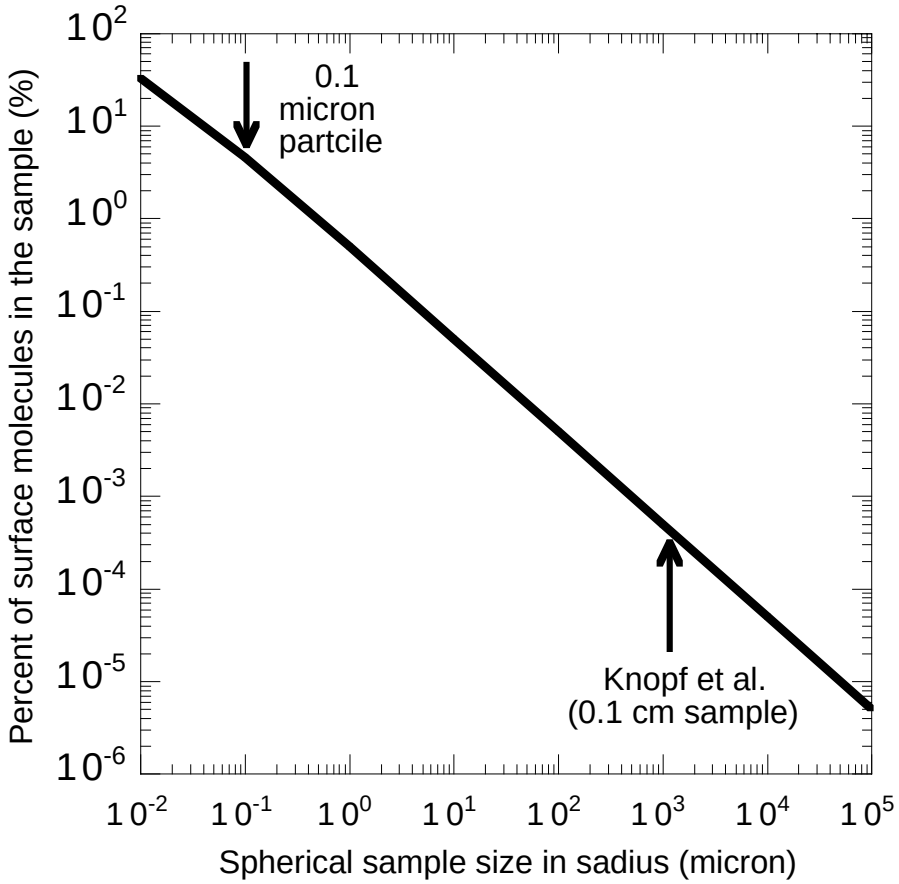

Fig. 1. The percentage of molecules residing on the surface for a given size sample. To calculate the number of molecules in the bulk a density of 1.3 g cm^{-3} was assumed. A molecular weight of 63 g mol^{-1} was used in the bulk calculations. To calculate the number of molecules on the surface a site density of 1015 cm^{-2} was assumed.

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